# Growth kinetics of quasicrystalline and polytetrahedral phases of Al-Pd-Mn, Al-Co, and Al-Fe from the undercooled melt

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Melts of the alloys Al-Pd-Mn, Al-Co, and Al-Fe are containerlessly undercooled and solidified using the technique of electromagnetic levitation. The (quasi)crystal growth velocity is measured as a function of undercooling for the various phases by a high-speed infrared photosensing device. Additionally, a video image technique is applied to measure growth velocities especially at low undercoolings where sluggish growth prevails. Scanning and transmission electron microscopy as well as x-ray diffraction is utilized to identify the phases primarily solidified from distinct levels of undercooling. The experimental results are analyzed within current theories of dendritic growth. The investigations give insight into topological and chemical short-range order effects in the growth kinetics of phases with polytetrahedral ordering in the solid state.

## I. INTRODUCTION

The difference in the Gibbs free energy between the stable solid phase and the undercooled melt gives access to the formation of a great variety of metastable materials.[1] They range from structurally metastable phases, supersaturated grain-refined alloys, disordered superlattice structures even up to amorphous phases. The formation of metastable materials from the undercooled melt is controlled by crystal nucleation and subsequent crystal growth. Nucleation often preselects the structure of the solid phases, stable or metastable, formed during solidification (see, e.g., Refs. 2 and 3) while crystal growth preponderantly governs the evolution of different metastable microstructures.[4]

Recently, experimental techniques have been developed for undercooling of bulk melts in a containerless state. The application of electromagnetic levitation provides a freely suspended drop at which nonequilibrium processes during solidification are directly observable.[5] In particular a technique has been developed to measure the growth velocity as a function of undercooling on bulk samples containerlessly processed and undercooled by electromagnetic levitation. In such a way a variety of physical phenomena has been investigated occurring during nonequilibrium solidification of undercooled melts. The validity of the assumption of collision-limited growth[6] has been verified for undercooled melts of pure metals and solid solutions.[7] Critical undercoolings have been determined for the onset of solute trapping in dilute alloys of Ni-B and Ni-Zr,[8,9] and disorder trapping in intermetallics,[10] for microstructural transitions of coarse-grained dendritic to equiaxed grain-refined alloys,[11] and even faceted to nonfaceted microstructural transitions in semiconductors.[12]

All these investigations concern crystalline states of matter. On the other hand, studies on quasicrystals have attracted much attention since their discovery in 1984.[13] In previous work it was shown that bulk melts of Al-based alloys forming quasicrystalline and polytetrahedral phases could be undercooled employing the electromagnetic levitation technique. This has led to progress in the understanding of the structure dependence of nucleation processes and its impact on the formation of solid phases with different topological structures.[14,15,16] In these studies the growth velocity, $V$, during solidification of undercooled melts of quasicrystalline and polytetrahedral phases was roughly estimated to be in the order of magnitude of $V \approx 1$ cm/s at the maximum levels of undercooling achieved.[14–17] However, there is still a lack of detailed studies on the kinetics of growth of quasicrystalline and polytetrahedral phases as a function of undercooling.

In the present contribution we report on measurements of the growth velocity of different quasicrystalline and polytetrahedral phases as a function of the undercooling. The growth kinetics of two different quasicrystalline phases was investigated: a stable icosahedral phase ($I$ phase) with quasiperiodicity in three dimensions which forms in Al-Pd-Mn,[18] and a metastable decagonal phase ($D$ phase) with quasiperiodicity in two dimensions in Al-Co.[19] The alloy compositions were selected such as to ensure the primary solidification of the quasicrystalline phases. In the case of Al-Pd-Mn,

 

samples of the composition $Al_{72}Pd_{21}Mn_7$ were chosen, a composition at which a two-phase equilibrium between the *I* phase and the melt exists.[20,21] For Al-Co, splat-cooling experiments[22] have shown that the composition of the *D* phase is nearby the concentration of $Al_{73}Co_{27}$. In order to circumvent the primary formation of the CsCl-type $\beta$ phase, a slightly different alloy composition of $Al_{74}Co_{26}$ was selected.[3] In addition, Al-Fe alloys were studied which form crystalline polytetrahedral phases. We investigated the growth kinetics of the monoclinic phase $\lambda$-$Al_{13}Fe_4$ with 102 atoms per unit cell[23] and the orthorhombic phase $\mu$-$Al_5Fe_2$ with 15 atoms in its unit cell[24] in alloys of the stoichiometric compositions of these phases.

The results of the measurements of the growth velocity as a function of undercooling were analyzed within current theories of dendritic growth. The analysis provides information on the attachment kinetics of atoms transferring from the liquid to the solid-liquid interface. Moreover, it gives insight into the dependence of the growth kinetics on the chemical and topological short-range order of the crystalline and quasicrystalline solids formed from the undercooled melt.

## II. EXPERIMENT

Al-Fe, Al-Co, and Al-Pd-Mn alloys were prepared by inductively premelting the constituents (purity better than 99.99%) under an Ar atmosphere in a water-cooled copper crucible. Bulk specimens of about 1 g in mass were melted, undercooled and containerlessly solidified by electromagnetic levitation.[5] The ultrahigh-vacuum levitation chamber was evacuated to a pressure of $10^{-7}$ mbar and subsequently backfilled with ultrahigh-purity He+20%$H_2$ gas prior to the levitation experiment. The temperature of the sample was measured by a pyrometer with an absolute accuracy of $\pm 5$ K at a sampling rate of 100 Hz.

The growth velocity as a function of undercooling was determined making use of two different techniques. A high-speed infrared photosensing device was applied for the time-resolved measurements of the rapid temperature rise during recalescence with a time resolution better than 1 $\mu$s.[25] This technique is based upon the assumption that the solidification front is described by the envelope of the growing dendrites. This assumption is justified at medium and large undercoolings.

However, it becomes less accurate for small undercoolings at which dendrites are large and their growth kinetics becomes sluggish.[26] Therefore, growth velocities were alternatively measured by a video technique. This setup is schematically shown in Fig. 1(a). Nucleation was externally triggered by touching the droplet at a preselected undercooling level with an $Al_2O_3$ needle. The solidification front propagates from the nucleation point through the volume of the undercooled melt. A steep temperature gradient ahead of the solid-liquid interface is established due to the release of the heat of fusion at the solidification front. This temperature gradient leads to a sharp contrast in the brightness of the sample which is detectable with an optical video system. A video recorder in combination with a CCD camera was used to record the continuous propagation of the solidification front in the undercooled melt with a time resolution of 0.01 s. Figure 1(b) illustrates schematically a temperature-time

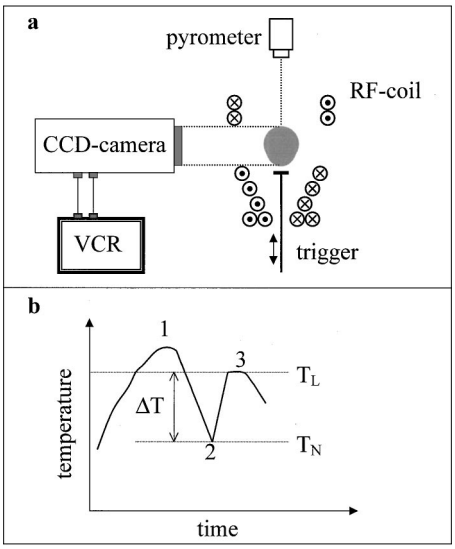


FIG. 1. Experimental setup to measure the growth velocity as a function of undercooling with a CCD camera (a). The sample is levitated and heated within the RF coil. A pyrometer monitors the temperature of the sample during the entire experiment with a sampling rate of 100 Hz resulting in a temperature-time profile (b). The undercooling is determined from the temperature-time profiles as the difference between the liquidus temperature, $T_L$, and the nucleation temperature, $T_N$. The sample is heated above $T_L$ (point 1) and subsequently cooled into the metastable undercooled liquid region. At a preselected temperature (point 2) the nucleation of the melt is externally triggered by touching the liquid sample with an $Al_2O_3$ trigger. The solidification front propagates from the nucleation point into the undercooled melt. A steep temperature gradient ahead of the solid-liquid interface is established due to the release of the heat of fusion at the solidification front. This temperature gradient is monitored by the CCD camera (between points 2 and 3).

profile as measured by a pyrometer during heating, melting, overheating (1), undercooling (2), and solidification (3) of a levitated drop. The undercooling $\Delta T = T_L - T_N$ ($T_L$: liquidus temperature of the respective solid phases; $T_N$: nucleation temperature at which solidification starts) is inferred from such temperature-time profiles.

Figure 2 shows the sequence of images recorded with this setup for the solidification of the decagonal *D* phase from an $Al_{74}Co_{26}$ melt which was undercooled by 160 K. The crystallization time is determined by counting the number of images taken from the detection of the onset of solidification to complete solidification of the sample divided by the sampling rate. The growth velocity is then given by dividing the diameter, *D*, of the sample by the crystallization time.

In the investigated regime of growth velocities the dominant contribution to the error, $\Delta V$, of the measured growth velocity is due to the limited sampling rate, $v$. It can be estimated by

$$\frac{\Delta V}{V} = \frac{V}{Dv}. \tag{1}$$

Thus, with typical sample diameters of $D \approx 7$ mm, and a sampling rates of 100 Hz, the error in the measurement of $V$

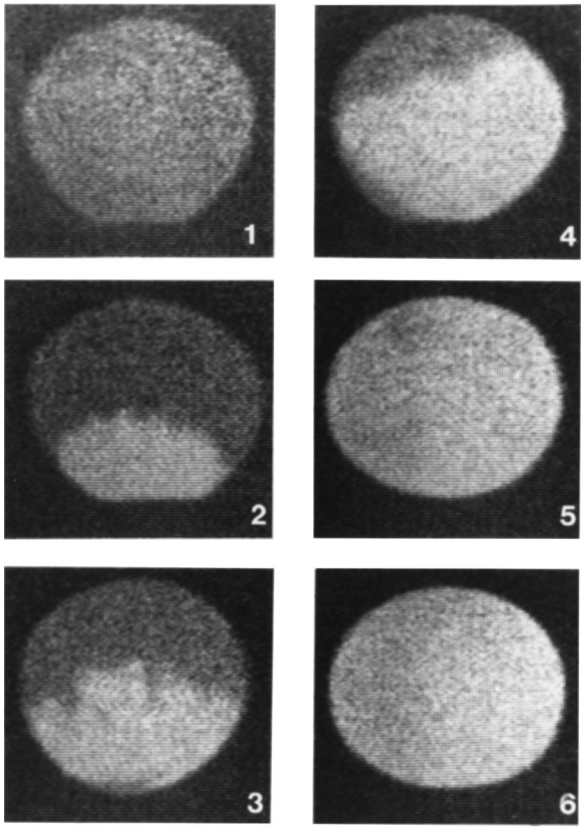


FIG. 2. Images of the solidification front as recorded during solidification of the decagonal $D$ phase from an Al-Co melt undercooled by 160 K by using a CCD camera and a video recorder with a frame frequency of 50 Hz. The solidified phase is heated up by the release of the heat of crystallization. It therefore appears as a bright region compared to the dark region of the undercooled melt.

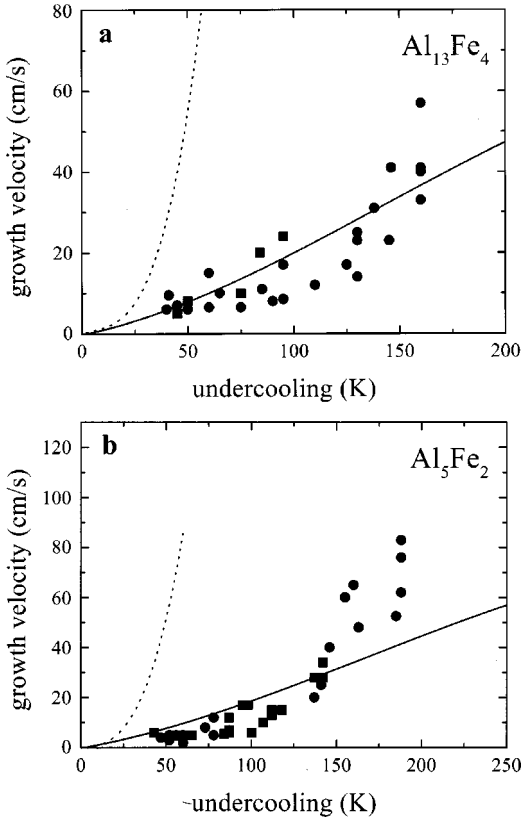


FIG. 3. Growth velocity $V$ as a function of undercooling $\Delta T$ for the polytetrahedral λ phase solidified from an $Al_{13}Fe_4$ melt (a) and the polytetrahedral $\mu$ phase formed from an $Al_5Fe_2$ melt (b). ■: measured by the CCD camera; ●: measured by the photosensing device. Prediction of the dendrite growth model for collision-limited growth (− − −) and diffusion-controlled growth (—).

is less than 30%, if $V<0.2$ m/s. For the measurement of greater growth velocities the high-speed photosensing device was used.

## III. RESULTS

Investigations by x-ray diffraction, scanning and transmission electron microscopy on the as-solidified samples were performed to identify the phases primarily solidified from melts of the different alloys at various levels of undercooling. The result is that for all levels of undercooling the λ phase solidifies primarily from the melt of composition $Al_{13}Fe_4$ and the $\mu$ phase from the melt of composition $Al_5Fe_2$. The results of equivalent investigations previously performed[3] on Al-Co alloys showed that the metastable $D$ phase solidifies primarily from $Al_{74}Co_{26}$ melts provided the undercooling exceeds 120 K. For $\Delta T<100$ K, a cubic $\beta$ phase nucleates primarily from the $Al_{74}Co_{26}$ melt. Correspondingly, it is found that for all levels of undercooling the icosahedral $I$ phase solidifies primarily from the $Al_{72}Pd_{21}Mn_7$ melt.

Figure 3 depicts the growth velocity, $V$, as a function of undercooling measured on $Al_{13}Fe_4$ alloy (a) and $Al_5Fe_2$ alloy (b). The data obtained from the photosensing device (full circles) and the video technique (full squares) are in good agreement within the experimental scatter in the undercooling range in which both techniques were applied. The growth velocity of the λ phase [Fig. 3(a)] rises by one order of magnitude from 5 cm/s for an undercooling of $\Delta T^{\lambda}=T_L(\lambda)-T_N=40$ K [$T_L(\lambda)$: liquidus temperature of the λ phase] to 50 cm/s for the maximum undercooling of $\Delta T^{\lambda}=160$ K. The growth velocity of the $\mu$ phase increases from 5 cm/s for an undercooling of $\Delta T^{\mu}=T_L(\mu)-T_N=40$ K [$T_L(\mu)$: liquidus temperature of the $\mu$ phase] to 85 cm/s for the maximum level of undercooling of $\Delta T^{\mu}=190$ K.

Figure 4 shows the growth velocity as a function of the undercooling for the quasicrystalline phases. The growth velocity of the $I$ phase in Al-Pd-Mn [Fig. 4(a)] rises slowly from 3 cm/s ($\Delta T^I=20$ K) to approximately 10 cm/s ($\Delta T^I=125$ K). Figure 4(b) exhibits $V(\Delta T)$ for the $D$ phase in the $Al_{74}Co_{26}$ alloy. It increases from 10 cm/s at $\Delta T^D=120$ K to approximately 20 cm/s at the largest undercooling of $\Delta T^D=200$ K.

## IV. DISCUSSION

The growth velocities of the quasicrystalline phases and the polytetrahedral phases are smaller by one to two orders of magnitude if compared with the growth velocities measured in pure metals and binary solid solutions.[7]

For the analysis of growth behavior we refer to current models developed to describe dendritic growth in undercooled melts. The negative temperature gradient into the un-

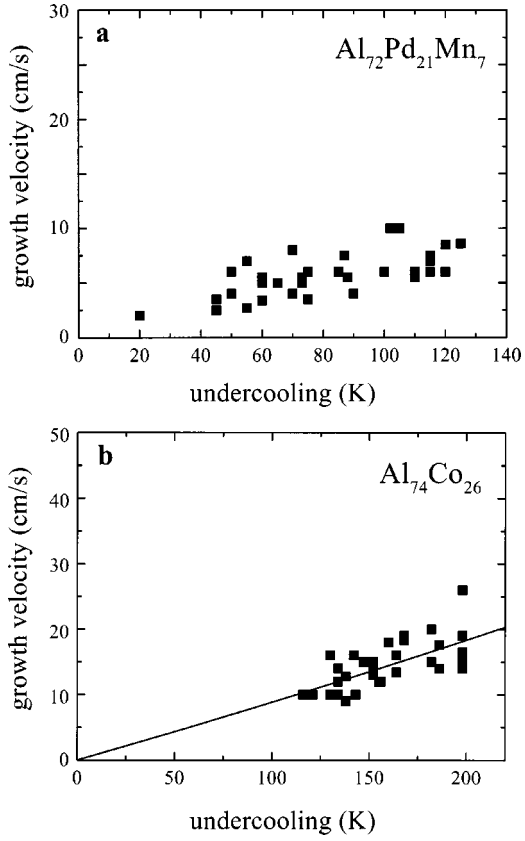


FIG. 4. Growth velocity $V$ as a function of undercooling $\Delta T$ for the icosahedral $I$ phase solidified from an $Al_{72}Pd_{21}Mn_7$ melt (a) and the metastable decagonal $D$ phase formed from an $Al_{74}Co_{26}$ melt (b). Data were measured by the CCD camera (■). The solid line represents the prediction of the dendrite growth model on the assumption of diffusion-controlled growth.

dercooled melt due to the instantaneous release of the heat of crystallization at the solid-liquid interface destabilizes the planar solidification front and leads to dendritic growth modes.[27] According to the Lipton-Kurz-Trivedi (LKT) model[28] the total undercooling $\Delta T = T_L - T_N$ measured in the experiments consists of various individual contributions:

$$\Delta T = \Delta T_t + \Delta T_r + \Delta T_k + \Delta T_c, \tag{2}$$

with $\Delta T_t$, $\Delta T_r$, $\Delta T_k$, and $\Delta T_c$ being the thermal, curvature, kinetic, and constitutional undercooling, respectively. The thermal undercooling results from the solution of the heat transport equation

$$\Delta T_t = T_i - T_N = \frac{\Delta H_f}{c_p^L} I\nu(P_t). \tag{3}$$

$T_i$ denotes the temperature at the solid-liquid interface, $\Delta H_f$ the heat of fusion, $c_p^L$ the specific heat of the undercooled melt, $I\nu$ the Ivantsov function, $P_t = VR/2a$ the thermal Péclet number, $R$ the dendrite tip radius, and $a$ the thermal diffusivity.

The curvature undercooling takes into account the depression of the melting temperature due to the curvature of the solid-liquid interface as described by the Gibbs-Thomson effect. It is given by

$$\Delta T_r = 2\frac{\Gamma}{R}, \tag{4}$$

where $\Gamma = \sigma/\Delta S_f$ is the Gibbs-Thomson coefficient with the entropy of fusion, $\Delta S_f$, and the solid-liquid interfacial energy, $\sigma$.

The constitutional undercooling, $\Delta T_c$, is neglected for the calculation of the dendrite growth velocity of the binary alloys since the polytetrahedral λ and $\mu$ phases exhibit a congruent melting behavior as observed in the respective temperature-time profiles of each heating and cooling cycle. Thus liquidus and solidus temperatures coincide and, consequently, the constitutional undercooling will be zero. For the metastable quasicrystalline $D$ phase, studies of the metastable phase diagram have shown that the $D$ phase exists in a very narrow concentration range, around the concentration of $Al_{74}Co_{26}$ alloy, quite similar to an intermetallic phase with a steep minimum in the Gibbs free energy versus concentration function.[22] Since the $D$ phase forms from a melt with the same composition at the concentration $Al_{74}Co_{26}$, the contribution of constitutional undercooling to the total undercooling will be small compared to the thermal undercooling term for the metastable $D$ phase in $Al_{74}Co_{26}$ and it can therefore be neglected. The constitutional contribution cannot be calculated for the ternary alloy $Al_{72}Pd_{21}Mn_7$ since the LKT model of dendritic growth allows the calculation of $\Delta T_c$ for binary alloys only.

Deviations from local equilibrium at the solid-liquid interface are taken into consideration by the kinetic undercooling $\Delta T_k = T_L - \Delta T_r - T_i$. Following the rate theory of crystal growth,[29] $\Delta T_k$ is determined by calculating the transition rates of atoms going from the liquid to the solid state, $R_L$, and the rate of atoms going from the solid to the liquid state, $R_S$, thus $V = \delta(R_L - R_S)$. The interface thickness $\delta$ for quasicrystalline and polytetrahedral phases is assumed to be one interatomic spacing, a value which is taken from a numerical construction of the solid-liquid interface for several polytetrahedral phases.[16] This yields

$$V(T) = V_c\left[1 - \exp\left(-\frac{\Delta G}{k_B T}\right)\right], \tag{5}$$

where $k_B$ denotes Boltzmann's constant and $\Delta G$ the difference in Gibbs free energy of the solid and the liquid phase. For the calculation of $\Delta G$ the validity of the linear approximation[30] is assumed hence $\Delta G = \Delta H_f \Delta T_k / T_L$. If the atomic attachment kinetics at the interface is collision-limited,[6] the prefactor $V_c$ corresponds to the speed of sound $V_s$ as an ultimate upper limit of the dendrite growth velocity.[31] This means that the attachment kinetics of atoms from the liquid onto the interface is governed by the atomic vibrational frequency $\nu_0 = k_B T/h$, which is of the order of $10^{13}$ Hz ($h$ is Planck's constant). This results in a kinetic undercooling $\Delta T_k \approx V/\mu$ with $V$ being the measured growth velocity and $\mu$ the kinetic growth coefficient

$$\mu = f\frac{\Delta H_f V_S}{k_B T_L^2}. \tag{6}$$

$f$ denotes the fraction of interfacial sites at which attachment of atoms can occur. This factor was set to unity in the cal-

culation of the growth velocity. The conditions of collision-limited growth have been shown to prevail in pure Ni melts and solid solutions.[7]

On the other hand, the growth of a superlattice structure in intermetallic compounds requires short-range atomic diffusion. Hence, it is expected that the interface undercooling of intermetallics is governed by short-range atomic diffusion, since the atoms must sort themselves out onto the various sublattices.[10,32] In this case where the atomic attachment kinetics is controlled by atomic diffusion processes, the prefactor $V_c$ of Eq. (5) is given by the atomic diffusion speed $V_d$. The speed of sound in liquid metals is about two or three orders of magnitude larger than the diffusion speed. Therefore, the kinetic undercooling $\Delta T_k$ is much larger than in the case of collision-limited growth,[10] which leads to a lower growth velocity for diffusion-controlled growth than for collision-limited growth.

Equation (3) gives the relationship between the thermal undercooling, $\Delta T_t$, and the product of $V$ times $R$ in terms of the thermal Péclet number $P_t$. For a unique calculation of $V$ as a function of $\Delta T_t$ the criterion of marginal stability[33] is utilized, which yields an expression for the dendrite tip radius $R$

$$R = \frac{\Gamma/\sigma^*}{P_t \frac{\Delta H_f}{c_p^l}(1-n)}, \tag{7}$$

with

$$n = \frac{1}{\sqrt{1+\frac{1}{\sigma^* P_t^2}}},$$

where $\sigma^* = 1/(4\pi^2)$ is the stability parameter.

Previous measurements of the dendrite growth velocities on undercooled pure metals and solid solutions show that the experimentally determined growth velocity–undercooling relation is well described within dendrite growth theory.[7] Calculations of the dendrite growth velocity as a function of undercooling were performed on the basis of Eqs. (2) to (7) using the data of the alloy parameter as listed in Table I.

Results of the calculations of the dendrite growth velocity for the crystalline polytetrahedral phases are shown in Fig. 3(a) for λ phase and in Fig. 3(b) for $\mu$ phase. The dashed line represents the results as calculated on the assumption of collision-limited growth while the solid line gives corresponding data obtained on the assumption of diffusion-limited growth. A comparison of the experimental data with the predictions of the LKT model under the two different assumptions leads to the conclusion that dendrite growth of solid phases with polytetrahedral short-range order is diffusion-controlled and much slower than expected for collision-limited growth. From the calculations of the growth velocity–undercooling relations a value for the average atomic diffusion speed is estimated from the best fit to the experimental results yielding $V_d = 3$ m/s. A similar value of $V_d = 6.7$ m/s was reported by Smith and Aziz for dilute Al-Cu alloys as measured by surface resolidification experiments.[34] The analysis of the growth behavior of the quasicrystalline $D$ phase in $Al_{74}Co_{26}$ alloy within the LKT model leads to a similar conclusion but with a value for the atomic diffusion speed of $V_d = 2$ m/s, which is smaller than $V_d$ of the $\mu$ and λ phase of Al-Fe.

TABLE I. Material parameters used for the calculation of the growth velocity as a function of undercooling. $V_d$ is chosen in such a way as to give the best fit to the experimental results.

| Parameter | Dimension | λ phase | $\mu$ phase | $D$ phase |
|---|---|---|---|---|
| $\Delta H_f$ | kJ/mol | 19[a] | 19,7[a] | 16,7[a] |
| $c_P^L$ | J/(K mol) | 50[b] | 50[b] | 50[b] |
| $T_L$ | K | 1420[a] | 1430[a] | 1440[a] |
| $V_S$ | m/s | 4000[c] | 4000[c] | 4000[c] |
| $\alpha$ | $m^2/s$ | $5\times10^{-6}$[d] | $5\times10^{-6}$[d] | $5\times10^{-6}$[d] |
| $\sigma$ | $J/m^2$ | 0.16[a] | 0.17[a] | 0.16[a] |
| $\gamma$ | K m | $1\times10^{-7}$ | $1.2\times10^{-7}$ | $1.2\times10^{-7}$ |
| $V_d$ | m/s | 3 | 3 | 2 |

[a]Values taken from Refs. 15 and 39.
[b]Determined by DTA for $Al_{62.5}Cu_{25.5}Fe_{12}$ and $Al_{66}Cu_{17}Co_{17}$ melts (Ref. 17).
[c]Typical value for liquid metals (Ref. 40).
[d]Typical value for liquid metals (Ref. 41).

The growth kinetics of phases with polytetrahedral short-range order, though even more sluggish, behaves analogously to the growth kinetics of some intermetallic compounds. For example, measurements of the growth velocity $V$ in the Al-Ni system show that the chemically ordered $\beta$ phase grows significantly more slowly ($V = 2$ m/s, $\Delta T = 220$ K) than the disordered solid solution $\gamma$ ($V = 12$ m/s, $\Delta T = 220$ K).[32] This difference is explained by the chemical ordering of the intermetallic compound. The atoms in the liquid cannot occupy each crystal site but have to find their correct superlattice sites. This requires short-range diffusion of the atoms at the solid-liquid interface and consequently the growth kinetics is controlled by a diffusion-limited growth process.

In the case of the $D$ phase the predictions of the LKT theory lead to good agreement with the experimental results, while for both Al-Fe alloys only fair agreement between theory and experiment was obtained. In the latter case, at undercoolings below 130 K, growth velocities were measured comparable to those for the $D$ phase. At higher undercooling a rapid rise of the growth velocities is observed, which is comparable to that estimated for collision-limited growth. This may indicate a change in the growth mechanism of the λ and $\mu$ phase at a critical undercooling of about 130 K. Due to the fact that λ and $\mu$ phase are chemically highly ordered phases it might be speculated whether a disorder-trapping phenomenon is responsible for this behavior. For the intermetallic compound CoSi,[10] although at considerably larger critical growth velocities, this phenomenon was experimentally observed.

Growth velocities of the λ phase in ternary Al-Cu-Fe and the $D$ phase in Al-Cu-Co alloys were reported in Refs. 14, 15, 17. In specimens of the composition $Al_{65}Cu_{25}Co_{10}$ a $D$ phase of the composition of $Al_{67}Cu_{16}Co_{17}$ grows at a velocity of $V \approx 0.8$ cm/s at a relative undercooling of $\Delta T/T_L = 0.16$. In $Al_{64}Cu_{22}Co_{14}$ samples a $D$ phase of the composition $Al_{67}Cu_{14}Co_{19}$ grows at $V \approx 1.4$ cm/s at a relative undercooling of $\Delta T/T_L = 0.15$. For λ-$(Al, Cu)_{13}Fe_4$ solidifying pri-

marily in $Al_{62}Cu_{25.5}Fe_{12.5}$ specimens, growth velocities of $V \approx 1.4$ cm/s at a relative undercooling of $\Delta T/T_L = 0.14$ were measured. These growth velocities are about one order of magnitude lower than measured for the same phases in the congruently melting binary alloys.

Very small growth velocities of $V \approx 0.5$ cm/s were measured at a relative undercooling of $\Delta T/T_L = 0.1$ for the *I* phase of the composition $Al_{64}Cu_{23}Fe_{13}$ and $Al_{63}Cu_{21}Fe_{16}$ solidifying in samples of the compositions $Al_{60}Cu_{34}Fe_6$ and $Al_{58}Cu_{34}Fe_8$, respectively (note the large difference of the compositions of solid and liquid).[14,15,17]

The drastically reduced growth velocities of the incongruently melting ternary alloys may be a result of constitutional undercooling, which leads to a decrease of the dendrite growth velocity if as solute trapping does not play a significant role.[8,9] Presently, attempts are being undertaken to extend dendrite growth theory to multicomponent alloys,[35] which may open up the way to quantitatively determining the constitutional undercooling and thus $V_d$ of the *I* phase in Al-Pd-Mn whose ternary phase diagram is well investigated.[20]

Moreover, from the point of view of the attachment kinetics at the interface it must be considered that the polytetrahedral and quasicrystalline alloys exhibit a complex chemical structure in which a given atomic site can only be occupied by one kind of atomic species. In general, the probability that an atom of the right species will attempt to attach to a specific site of the ordered solid is the lower, the larger the number of components of the alloy. The attachment probability also decreases if the composition of the melt deviates from that of the solid, which is the case for all the above-mentioned ternary alloys. In these cases, not diffusion over one interatomic spacing, as for binary intermetallic compounds of equiatomic composition, but diffusion over more than one interatomic distance is required for the growth of the polytetrahedral and quasicrystalline phases. This again leads to a decrease of the growth velocity.

Despite these aspects concerned with the chemical structure, quasicrystalline and polytetrahedral phases are characterized by a complex polytetrahedral topological structure. Modeling of the solid-liquid interface[16] revealed a low number of atoms in the solid-liquid interface compared with that for crystals with fcc, hcp,[36] or bcc (Ref. 37) structure. This means that the number of sites at which attachment can occur is small for the polytetrahedral and quasicrystalline phases compared with simple crystalline structures such as fcc or bcc. Thus, the factor *f* which was set to unity in Eq. (6) may become less than 1 and as a result the kinetic undercooling increases. Such an effect is well known in solidification of undercooled melts of semiconductors such as pure Ge and dilute Ge-Sn alloys,[38] which show metallic behavior in the liquid with more or less isotropic bonds and semiconducting behavior in the solid with strongly directional covalent bonds. An atomic site factor less than unity might lead to sluggish growth kinetics of the polytetrahedral and quasicrystalline phases. Diffusion of atoms to or within the interface is necessary to build up the complex chemical structure of the polytetrahedral and quasicrystalline phases.

The characteristic timescale needed for such atomic diffusion processes is about three orders of magnitude larger than the typical time period of the atomic vibrations, which is comparable to the reciprocal Debye frequency ($10^{-13}$ s). Therefore, the site factor *f* controlled by topological effects [Eq. (6)] will only lead to a significant influence on the attachment kinetics of atoms at the solid-liquid interface if it is in the order of $10^{-3}$ or even less. This may explain the experimental findings that the $\lambda$ and $\mu$ phases of the binary alloys of Al-Fe exhibit essentially the same growth velocity at the same level of undercooling although they have different crystal structures and hence different structural topology. Furthermore, the growth kinetics of *D* phase in Al-Co alloy is similar to that of $\lambda$ and $\mu$ phase even though their structural topology differs from that of the quasicrystalline *D* phase. This is valid in the undercooling range where the growth kinetics of all phases is controlled by atomic diffusion ($\Delta T < 130$ K).

## V. CONCLUSIONS

The growth velocity was measured as a function of undercooling for several polytetrahedral and quasicrystalline phases. The experimental results were discussed within current models of dendritic growth. The analysis indicates that the growth kinetics of all investigated phases is diffusion-controlled. The experiments highlight the fact that the growth of the investigated phases is dominated by the chemical short-range order of the solids and the chemical composition of the liquid. Any change of the topological short-range order appears to be of minor importance for the growth kinetics. This behavior is in contrast to that of the nucleation processes of polytetrahedral and quasicrystalline phases in undercooled melts, which are dominated by effects of the topological structure, while the effect of the chemical composition turned out to be negligible.[16]

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